A PHASE-RULE STUDY
of
SODIUM NITRATE
SODIUM IODATE, AND WATER
as a Three-Component System

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[Contribution from the Chemical Laboratories of New York University]

TERNARY SYSTEMS. IX. SODIUM IODATE, SODIUM NITRATE AND WATER[1]

By Arthur E. Hill and John E. Donovan

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In the Caliche from which Chile saltpeter is extracted there are present a number of salt-forming ions. Of the many poly-component systems which these may compose with water a number have been investigated but a very large number still remain without published investigation. A short time ago it was decided to investigate some of these three-component and four-component systems at New York University. During the process of this work, there appeared the investigations by Foote and Vance,[2] covering the system sodium iodate, sodium nitrate and water at various temperatures between the ternary eutectic and 35°. Our own work on this system, nearly completed before Foote and Vance's became known to us, contains certain isotherms at temperatures slightly different from those selected by Foote and Vance, and at a duplicate temperature in the case of the 25° isotherm. Our findings are in general accord with those of the earlier publication; the two sets of investigations gave a rather unusually complete set of data for a ternary system. To the earlier isotherms at 0, 8, 25 and 35° we add as new material the isotherms at 5 and at 50°.

Attainment of Equilibrium.—The solubility data on sodium iodate and water, previous to the work of Foote and Vance,[2] were both discordant and misleading, because of confusion as to the degree of hydration of the saturating salt (seven hydrates having been mentioned by various authors[3]) and also doubtless because of difficulties, which we shall point out, in the attainment of equilibrium. The stable hydrates found by us are in agreement with the findings of Foote and Vance, namely, $NaIO_3 \cdot 5H_2O$ below 20°, $NaIO_3 \cdot H_2O$ between 20 and 70°, above which temperature the anhydrous salt is stable in contact with solution. In the matter of attainment of equilibrium we have found the various alkali and alkaline-earth iodates to be extremely slow, as will be pointed out in later publications relative to the magnesium and potassium salts; and where in addition the formation of a hydrate is involved, as in the case of the sodium salt, the quantitative change to that form is also slow, giving most annoying retardation in the attainment of both internal and external equilibrium. We have given some considerable study to this problem and are in possession of the facts even though no remedy has been found outside of an extremely lengthy

[1] The material of this paper was presented by John E. Donovan in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Foote and Vance, *Am. J. Sci.*, **16**, 68 (1928); **18**, 375 (1929).

[3] See Mellor, "Comprehensive Treatise," Vol. II, p. 334.

agitation of the salt with water. The first very important finding is that if experiments are made with use of the anhydrous salt at any temperature at which a hydrate is the stable form, the equilibrium can be approached only from the side of supersaturation; samples treated with cold water and agitated at 25° showed a solubility of the order of 8.79% at the end of three hours, dropping slowly thereafter and remaining for many days above what we believe to be the true solubility for the hydrate. This behavior is undoubtedly owing to the higher solubility of the metastable anhydrous form, and to the fact that with samples of whatever amounts of solid phase were used, the process of solution was much more rapid than the process of hydration. In the endeavor to eliminate this source of error special experiments were conducted with the purpose of providing only pure hydrate as initial solid phase. It was found, however, that samples of supposed hydrate prepared by ordinary recrystallization in the neighborhood of 25° would regularly show the same phenomenon of forming supersaturated solutions, which may be again attributed to the presence of sufficient unhydrated salt to give the high results. It was only after a sample of the supposed hydrate had been agitated with new solvent three times and for a period of about two weeks at each treatment that it could be made to give results which could not be regarded as an approach from supersaturation. The elimination of this source of error, however, did not help with the second, which is the slow attainment of equilibrium. In only one instance have we been able to secure results, from true supersaturation and true undersaturation, which were within the limits of our analytical error, which for the determination of iodate by iodimetry we place at 0.2% as an extreme, and which probably is nearer 0.1%. The following results in Table I are typical.

TABLE I

$NaIO_3 + H_2O$ AT 25° (SOLID, $NaIO_3 + H_2O$)

Time	From undersaturation, %	From supersaturation, %	Difference in, %
3.5 hours	8.561	8.829	3.1
1 day	8.576	8.703	1.5
4 days	8.568	8.694	1.24
11 days	8.560	8.680	1.39
23 days	8.564	8.665	1.21

The two samples have remained more than 1% apart in solubility after twenty-three days, and show no marked trend after the fourth day. Similar results have been found in this Laboratory by Professor S. F. Brown and Mr. J. E. Ricci, in the course of investigations to be reported later. In one instance the solubility approached from supersaturation came down to 8.56% in thirty-five days; we therefore conclude that the figures from undersaturation, obtained after any briefer interval, are more nearly correct than those approached from supersaturation. We are quite unable to

agree with Foote and Vance that equilibrium from both directions has been reached, within narrow limits, in four to six hours, and raise the question as to whether their agreement between results from undersaturation and supersaturation at this temperature (8.65 and 8.66%) and at other temperatures may not be due to the use of anhydrous salt and the consequent agreement of two samples both from supersaturation. As a practical experimental matter, however, we have used the anhydrous salt as our original solid (this being necessary for our calculations in the ternary system) and have allowed a time of rotation from one week to two weeks; there is no evidence that longer periods, within reasonable limits, would add materially to the accuracy.

The Binary System, Sodium Iodate–Water.—For this work recrystallized and dehydrated salt in generous amount was put in 40-cc. glass-stoppered pyrex test-tubes and rotated in a water thermostat, constant to within 0.05°, for periods of about two weeks. The results are therefore those obtained from supersaturation, and are given in Table II.

TABLE II

SOLUBILITY OF $NaIO_3$ IN WATER

Temp., °C.	Wt., % of $NaIO_3$	Density of solution	Solid phase
5	3.30	1.028	$NaIO_3 \cdot 5H_2O$
15	5.85	1.051	$NaIO_3 \cdot 5H_2O$
20	7.81	...	$NaIO_3 \cdot H_2O + NaIO_3 \cdot 5H_2O$
22	8.11	1.071	$NaIO_3 \cdot H_2O$
25	8.67	1.077	$NaIO_3 \cdot H_2O$
35	10.58	1.093	$NaIO_3 \cdot H_2O$
40	11.70	...	$NaIO_3 \cdot H_2O$
50	13.95	...	$NaIO_3 \cdot H_2O$

These solubility data agree with those of Foote and Vance within 0.01 to 0.03% up to 40°, leading us to believe that their experiments were also done with the anhydrous salt and therefore represent approach to equilibrium from supersaturation. The densities are approximate figures, obtained by weighing the solution delivered by a calibrated 5-cc. pipet. The intersection of the two solubility curves, shown in Fig. 1, is at 20° within the accuracy of our measurements; this also is in accord with Foote and Vance's figure of 20.3° obtained by careful calculation from the logarithmic curves for the solubility against the inverse of the absolute temperature; their results by the thermal and dilatometric methods are about 0.5° lower. The composition of the hydrate stable at room temperature was determined by analysis for water content after samples slowly formed by isothermal evaporation had been brought to constant weight over the anhydrous form as desiccating agent in miniature desiccators; it gave 8.31% H_2O, 8.34% being required by the formula $NaIO_3 \cdot H_2O$. Difficulties in maintaining desiccators at the lower temperatures for the

pentahydrate were such that the crystallized salt was simply centrifuged well and analyzed directly; samples gave from 32.17 to 32.52% water, where 31.28% is required by the formula $NaIO_3 \cdot 5H_2O$. We confirm the findings of Foote and Vance that these are the only stable hydrates found in the temperature range studied, and that Meerburg's[4] formula $NaIO_3 \cdot {}^3/_2H_2O$ is not valid.

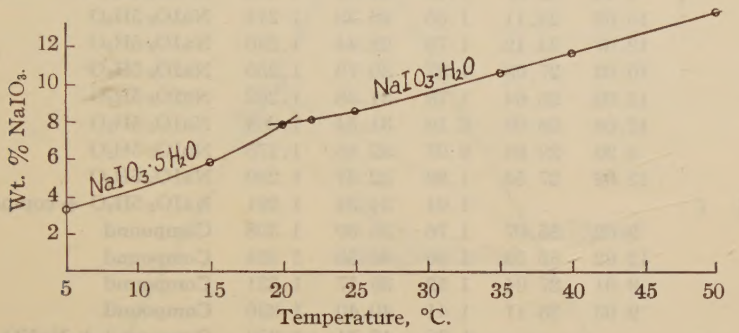

Fig. 1.—Solubility of sodium iodate in water.

The Ternary System.—For the study of the ternary system, good grades of sodium nitrate and sodium iodate were purified by crystallization. Weighed quantities of these salts were treated with weighed amounts of water in pyrex test-tubes and vigorously shaken by hand to prevent caking of the hydrate formed. The tubes were then slowly rotated in a water thermostat at the desired temperature for periods of about two weeks. After the tubes had been allowed to settle, samples were withdrawn into a calibrated pipet fitted with a small filter of absorbent cotton. One sample was weighed and evaporated in a platinum dish to constant weight at 110°, about twenty-four hours being required. From this the water content of the saturated solution became known. A second weighed sample was treated with potassium iodide and sulfuric acid and titrated with sodium thiosulfate solution, previously standardized against pure potassium iodate. The content of sodium iodate being thus established, the sodium nitrate was obtained by subtraction. The data at three temperatures are given in Table III, and plotted in Figs. 2, 3 and 4.

Since data were at hand both for the composition of the phase complex used and for the saturated solution, it was possible to extrapolate graphically or algebraically the line connecting these two points and thus determine approximately the composition of the solid phase, whenever it was a two-component body, by the intersection of this line with the side of the triangle. It was this procedure which first made clear to us, in the study of the 25° isotherm, that the solid phase is a monohydrate and not the more complex hydrate suggested by Meerburg. Following this method, two

[4] Meerburg, *Z. anorg. Chem.*, **45**, 324 (1905).

TABLE III

THE SYSTEM: $NaIO_3$–$NaNO_3$–H_2O

Temp., °C.	Point in diagram	Original Wt., % of $NaIO_3$	Complex Wt., % of $NaNO_3$	Saturated Solution Wt., % of $NaIO_3$	Saturated Solution Wt., % of $NaNO_3$	Density	Solid phase
	k	9.00	0.00	3.30	0.00	1.028	$NaIO_3 \cdot 5H_2O$
		9.02	4.00	1.58	4.50	1.042	$NaIO_3 \cdot 5H_2O$
		9.03	20.07	1.55	22.59	1.182	$NaIO_3 \cdot 5H_2O$
		10.05	23.11	1.65	26.38	1.214	$NaIO_3 \cdot 5H_2O$
		12.07	24.12	1.75	28.44	1.230	$NaIO_3 \cdot 5H_2O$
		10.03	27.08	1.87	30.70	1.255	$NaIO_3 \cdot 5H_2O$
		12.02	26.64	1.78	31.38	1.262	$NaIO_3 \cdot 5H_2O$
		12.04	28.09	2.10	31.54	1.263	$NaIO_3 \cdot 5H_2O$
		8.99	29.94	2.07	32.48	1.275	$NaIO_3 \cdot 5H_2O$
		12.02	27.54	1.86	32.37	1.269	$NaIO_3 \cdot 5H_2O$
5	f	...	...	1.94	34.34	1.291	$NaIO_3 \cdot 5H_2O$ + compound
		9.02	35.07	1.76	36.69	1.308	Compound
		12.02	35.55	1.60	38.38	1.324	Compound
		9.01	27.04	1.52	39.17	1.331	Compound
		9.03	38.11	1.41	40.40	1.336	Compound
	c	...	...	1.28	42.74	1.359	Compound + $NaNO_3$
		1.00	50.11	1.01	42.94	1.359	$NaNO_3$
	a	0.00	55.00	0.00	43.42	1.368	$NaNO_3$
	f	15.00	0.00	8.67	0.00	1.077	$NaIO_3 \cdot H_2O$
		9.60	2.89	6.38	3.26	1.078	$NaIO_3 \cdot H_2O$
		11.35	3.69	5.99	3.91	1.078	$NaIO_3 \cdot H_2O$
		9.01	7.01	4.80	7.32	1.092	$NaIO_3 \cdot H_2O$
		6.00	10.01	4.30	10.10	1.109	$NaIO_3 \cdot H_2O$
		4.00	16.01	3.68	16.08	1.149	$NaIO_3 \cdot H_2O$
25		9.10	18.19	3.41	19.47	1.171	$NaIO_3 \cdot H_2O$
		10.01	25.02	3.06	27.16	1.232	$NaIO_3 \cdot H_2O$
		10.01	30.02	2.84	32.67	1.276	$NaIO_3 \cdot H_2O$
		10.00	35.01	2.60	38.19	1.328	$NaIO_3 \cdot H_2O$
		10.04	41.15	2.31	45.12	1.392	$NaIO_3 \cdot H_2O$
	c	...	...	2.23	46.81	1.408	$NaIO_3 \cdot H_2O$ + $NaNO_3$
		0.92	55.36	1.09	47.44	1.396	$NaNO_3$
	a	.00	55.00	0.00	47.98	1.388	$NaNO_3$
	h	20.00	0.00	13.95	0.00	...	$NaIO_3 \cdot H_2O$
		19.05	5.02	9.63	5.74	...	$NaIO_3 \cdot H_2O$
		16.02	15.02	6.22	17.03	...	$NaIO_3 \cdot H_2O$
		14.08	25.14	4.82	28.18	...	$NaIO_3 \cdot H_2O$
		13.01	35.01	3.92	39.15	...	$NaIO_3 \cdot H_2O$
		12.99	35.97	4.00	39.94	...	$NaIO_3 \cdot H_2O$
50	f	...	...	3.84	41.53	...	$NaIO_3 \cdot H_2O$ + $NaIO_3$
		11.01	39.01	3.77	42.26	...	$NaIO_3$
		11.03	40.09	3.64	43.46	...	$NaIO_3$
		10.95	41.81	3.46	45.23	...	$NaIO_3$
		11.01	45.04	3.09	49.11	...	$NaIO_3$
	c	...	...	2.91	51.86	...	$NaIO_3$ + $NaNO_3$
		1.30	55.04	1.58	52.55	...	$NaNO_3$
	a	0.00	64.00	0.00	53.50	...	$NaNO_3$

points of interest were noted: first, that at 50° the anhydrous sodium iodate is solid phase in the solutions more highly concentrated with sodium nitrate, although the temperature is 20° below the transition temperature

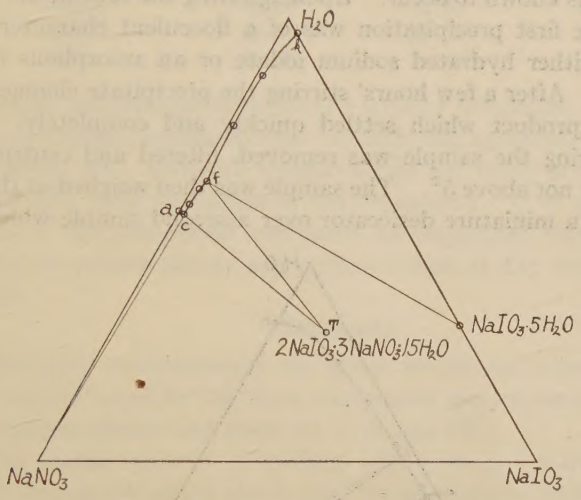

Fig. 2.—5° Isotherm: $NaIO_3$–$NaNO_3$–H_2O.

for that salt, as found by Foote and Vance; and, second, that at 5° a double salt exists, in contact with solutions of a restricted range of concentrations, as likewise reported by Foote and Vance for 8°.

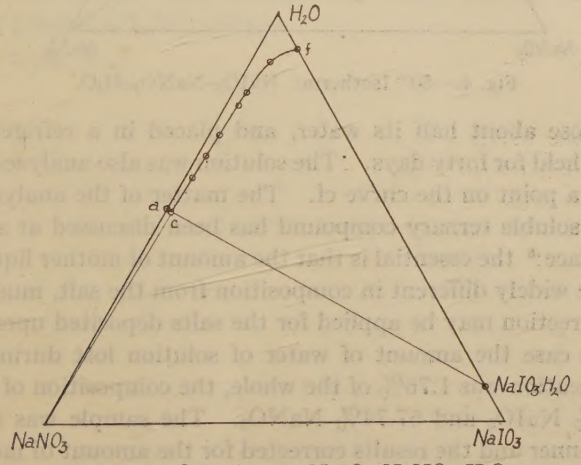

Fig. 3.—25° Isotherm: $NaIO_3$–$NaNO_3$–H_2O.

The Double Salt.—The double salt which appears in the 5° isotherm was prepared for analysis by making a complex of phases which fell within the triangle cTf of Fig. 2, bringing the solids completely into solution by

warming, and then allowing the solution to cool quietly to 5° without the formation of solid phase, which was not difficult because of the marked slowness with which precipitation of the iodate (and presumably of the double salt) is known to occur. Upon agitating the tube in the thermostat, however, the first precipitation was of a flocculent character, and must have been either hydrated sodium iodate or an amorphous form of the double salt. After a few hours' stirring the precipitate changed to a well-crystallized product which settled quickly and completely. After four days of stirring the sample was removed, filtered and centrifuged in an environment not above 5°. The sample was then weighed at this temperature, put in a miniature desiccator over a second sample which had been

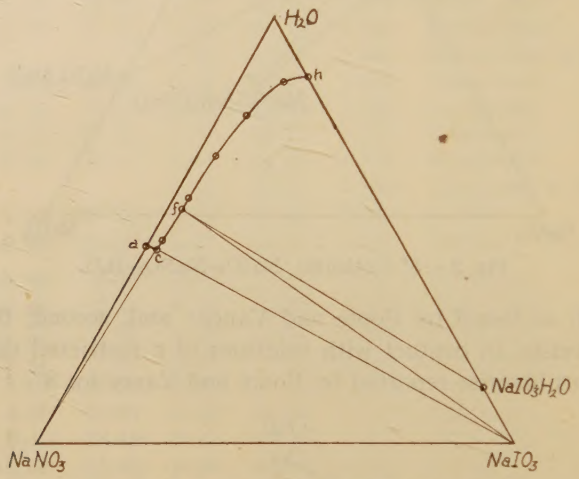

Fig. 4.—50° Isotherm: $NaIO_3$–$NaNO_3$–H_2O.

allowed to lose about half its water, and placed in a refrigerator at 7° where it was held for forty days. The solution was also analyzed and found to represent a point on the curve cf. The matter of the analysis of an incongruently soluble ternary compound has been discussed at some length in another place;[5] the essential is that the amount of mother liquor present, which is here widely different in composition from the salt, must be known so that a correction may be applied for the salts deposited upon its drying up. In this case the amount of water of solution lost during the forty days of desiccation was 1.76% of the whole, the composition of the mother liquor 1.40% $NaIO_3$ and 57.74% $NaNO_3$. The sample was analyzed in the usual manner and the results corrected for the amount of mother liquor present; the data are given in Table IV.

The result confirms the finding of Foote and Vance, with a somewhat better agreement between analysis and calculation.

[5] Hill, This Journal, 52, 3823 (1930).

TABLE IV

ANALYSIS OF TERNARY COMPOUND

	Uncorrected analysis, %	Corrected analysis, %	Calculated for $2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$
$NaIO_3$	42.06	42.60	42.97
$NaNO_3$	28.91	28.00	27.69
H_2O	29.03	29.40	29.34

The upper temperature limit for the ternary compound is at about 9.6°, as found by thermal measurements—in sufficient agreement with Foote and Vance's figure 9.8°, accurate measurements not being possible because of the apparently slow formation of the compound. It is obvious that the existence of this compound will have an important influence upon the separation of sodium nitrate and sodium iodate at any temperature below this point.

Summary

1. Solubility measurements are given for sodium iodate in water between 5 and 50°, and for the three-component system consisting of sodium iodate, sodium nitrate and water at 5, 25 and 50°.

2. The stable hydrates of sodium iodate are the pentahydrate below 20°, and the monohydrate above that temperature to its transition to the anhydrous form.

3. Hydrated sodium iodate does not reach equilibrium with its solution, from both undersaturation and supersaturation, within twenty-six days or more.

4. In the ternary system below 9.8° there exists a double salt of the formula $2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$.

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